

between the plurality of metallic alloy layers in an alternating manner comprises disposing the plurality of ceramic oxide layers adjacent to the surface of the substrate and between the plurality of metallic alloy layers in an alternating manner using a chemical vapor deposition technique.

41. (Original) The method of claim 22, wherein the substrate comprises at least one of a nickel-based superalloy, a cobalt-based superalloy, an iron-based superalloy, and an MCrAlY alloy, wherein M comprises at least one of nickel, cobalt, iron and a combination thereof.

42. (Original) The method of claim 22, further comprising the step of heat treating the nano-multilayered structure at a predetermined temperature.

43. (Original) The method of claim 42, wherein the predetermined temperature is in a range of between about 600°C to about 1400°C.

44. (Currently Amended) The method of claim 43, wherein the predetermined temperature is in a range of between about 600°C to about ~~1400°C~~ 900°C.

45. (Original) The method of claim 42, wherein the step of heat treating the nano-multilayered structure at a predetermined temperature comprises heat treating the nano-multilayered structure at a temperature of up to about 80% of the melting temperature of the nano-multilayered structure.

REMARKS/ARGUMENTS

Claims 1-45 are pending in the present Application. These claims stand rejected under various sections of the Patent Statute. Applicant submits that the changes presented herein, along with the accompanying remarks, should place the case in condition for allowance.

Some relatively minor deficiencies have been pointed out by the Examiner. The undersigned appreciates the attention to detail in this respect, and the appropriate changes have been made. Thus, the spelling error in claim 33 has been corrected. Moreover, claim 27 has been corrected, in order to overcome the objection to claim 28. The same range of thickness had been inadvertently recited in each claim. However, it appears that claim 27 should have recited a broader range. Applicant refers the Examiner to claims 6 and 7, which cover the same type of subject matter. Claim 6 provides some basis for the change to claim 27, and no issue of new matter is involved.

Applicant noted another minor claim error. Claims 43 and 44 appear to cover the same subject matter. Presumably, claim 44 was intended to recite a temperature range which was more specific than claim 43, and that range (600°C to about 900°C) has been incorporated into claim 44. Support for the change can be found, for example, in paragraph 16 of the specification (last sentence), and no issues of new matter are raised by this correction.

Rejections Under 35 U.S.C. 112

Claims 1-45 have been rejected under 35 U.S.C. 112, second paragraph, as being indefinite. A number of specific points are made by the Examiner, and they will generally be handled according to the sequence in the Office Action. The initial, specific rejection is directed to the term “nano-scale”. Applicant agrees that the term is not specifically defined in the specification. However, “nano-scale” is a term that is quite well-known in the art, and should not require a specific definition in the Application. In very general terms, “nano-scale” refers to a “sub-micron” scale, as the Examiner suggests, i.e., dimensions less than about 1 micron. Various references also point to a rough definition of about “1 to 100 nanometers”. However, the upper endpoint in such a definition is too restrictive for the present invention (e.g., see paragraph 14), since greater

dimensions are described in the specification and claims, e.g., about 200 nanometers (nm).

The Examiner also appears to question the absence of a lower endpoint for the “nano-scale” definition. However, Applicant believes the lower value for the term is also generally understood in the art. In reference to the Examiner’s other hypothetical questions, layers at the angstrom-scale, or the atomic scale, are not specifically excluded in the present invention. However, it would certainly be very difficult to detect and measure such layers by current analytical techniques. Moreover, the pending claims are directed to layers and structures “suitable for use in high-temperature applications”, and such a qualification does circumscribe a certain, minimum dimension. In summary, it is submitted that the “nano-scale” term in question is defined in a manner suitable enough for setting out the boundaries of the pending claims.

The Examiner also questions the metes and bounds of the term “metallic alloy layers”. Again, Applicant defers to some degree to the body of knowledge in the art. “Metals” and “metallic alloys” are terms which have been well-recognized for generations. Reference is made, for example, to non-limiting definitions provided in “Hawley’s Condensed Chemical Dictionary”, 14th Edition, 2001, John Wiley & Sons, Inc. (For example; see page 714 for a definition of “metal”, and page 36 for a definition of “alloy”).

The Examiner poses specific questions in regard to metals. Applicant submits that those skilled in the art understand that “metallic materials” could perhaps contain some non-metallic elements, but not to the extent which would cause one to characterize the entire material as “non-metallic”. Moreover, “alloys”, as described in the Hawley text, can be formed from two or more metals, or from a metal with a non-metal, e.g., carbon steel. Applicant certainly would agree with the Examiner that in some instances, the boundaries between definitions of materials (e.g., “metals” versus “non-metals”) is narrow. However, the definitions are still clear enough to provide suitable parameters for the present claims.

In paragraph II on page 3 of the Office Action, the Examiner questions use of the term “adjacent to the surface of the substrate”, e.g., as used in claim 22. Applicant responds that use of such a term is more of a style issue than a substantive issue. The term generally refers to layers being “disposed on” a substrate, as suggested by the Examiner. (See, for example, paragraph 16 of the specification, at about the 10th line, where “deposited on” is used). While it does not appear that the term was meant to specifically suggest the presence of an intervening layer between the lowest coating layer and the substrate, the possibility of such a layer is not specifically excluded either. The undersigned would be happy to review this particular point with the Examiner, and perhaps agree to suitable, alternative expressions.

In paragraph III of the Section 112 rejection, the Examiner also questions the use of the term “alternating manner”. On this point, Applicant submits that no possible ambiguity appears to exist. “Alternating” clearly means “every other one”, e.g., a type 1 layer, followed by a type 2 layer, followed by a type 1 layer, followed by a type 2 layer, etc. (Some variation in the composition for each particular type might also be possible). The questions posed by the Examiner in regard to variations on what could be termed “alternating” are not readily understood by the undersigned. While those questions seem to pose hypotheticals which are outside the normal meaning of the term in question, further discussion with the Examiner might prove helpful on this point.

Applicant is also unsure of the Examiner’s question concerning claim 42. The heat treatment in the claim is in fact a purposeful step undertaken in various embodiments of the claimed process. (See, e.g., paragraph 16 in the specification; penultimate sentence). Heating at a “predetermined” temperature simply means that the approximate temperature or temperature range is known beforehand, e.g., based on layer composition and the like. An exemplary predetermined range is provided in claims 43 and 44. Thus, the limitation in claim 42 should not be deemed superfluous.

On page 4 of the Office Action (paragraph V), the Examiner raises a number of points. First, the phrase “about 80% of the melting temperature...” is

questioned. In response, the undersigned notes that the “melting temperature” of the structure is based on the composition of the structure. In this context, the phrase in question does not appear to depend on whether or not a heat treatment has been performed on the structure beforehand.

However, the Examiner does raise a valid point regarding what material is being described in the context of “melting temperature”. While the language could perhaps have been more precise, its meaning is fairly well understood. In other words, “melting temperature” in this context would typically refer to the melting point of the lowest-melting component in the structure. (Those skilled in the art understand that this type of heat treatment is carried out at a temperature which is below that which would cause any degradation of the multilayer structure). In answer to the Examiner’s related question, there is no implication that the multilayer structure must somehow exhibit a single melting point.

The Examiner also questions the term “...about 80% of the melting temperature...”, in regard to the prescribed heat treatment. Under the assumption that the undersigned has adequately explained the “melting temperature” term in the preceding paragraph, the rest of claim 45 appears to be fairly clear. In other words, “80%” would represent approximately 80% of the numerical value for the melting temperature, according to the temperature scale used in the description, e.g., centigrade. Thus, for example, 80% of 1000°C would be about 800°C. The use of a percentage in this general context is generally accepted in the art. As an example, U.S. Patent 6,607,847 refers to high-temperature metal alloys which can be employed “...at approximately 80% or more of their melting temperatures, which are generally greater than about 1700°C.” (See column 1, lines 20-24). If any further discussion on this point is warranted (or on the other Section 112 issues), the undersigned would be willing to initiate a telephone call with the Examiner.

Rejections Under 35 U.S.C. 102

Claims 1, 4, 6, 8, 9, 12, 15, 17, 19, 22, 25, 29, 31, 32, 36, 37, 42, and 45 have been rejected under 35 U.S.C. 102(e). The reference applied in this anticipation rejection is U.S. Patent Application Publication 2004/0018393, filed for H. Fukui et al ("Fukui"). Applicant submits that these claims are in fact patentable over Fukui.

A brief discussion of the present invention would perhaps be helpful in clarifying the issues regarding the prior art. As described in the background section of the present Application, the nano-multilayered structure is an extremely useful system for protecting substrates employed in high-temperature applications. Gas turbine components, which are exposed to temperatures exceeding 1000°C, are excellent examples of such substrates. Typically, coating systems for protecting turbine blades and other components include an underlying metallic oxidation-resistant layer, such as "MCrAlY", or an aluminide material. A ceramic thermal barrier coating (TBC) (often formed from yttria-stabilized zirconia) is applied over the oxidation-resistant layer. The TBC provides the critical protection from the effects of high-temperature gas flow through the turbine.

As described in paragraphs 3 and 4 of the specification, coating systems of this type, while reliable and valuable for many end-use applications, may be deficient when challenged by the demands of future applications. For example, the MCrAlY coatings, while critical for oxidation resistance, do not have the enhanced wear resistance required for some applications. As is known in the art, these coatings are also not usually designed to have the required level of hardness, impact resistance, and erosion resistance at high temperatures. While the ceramic overlayer provides some of these characteristics, such as hardness, the other properties may be deficient for certain, specific end use applications.

Thus, a need for a balanced combination of relatively high-level physical and structural properties led to the discovery on which this invention is based. As described in paragraph 11 of the specification, the use of thin, alternating layers of metallic alloys and ceramic oxides can provide the desired combination of hardness, wear resistance, impact resistance, erosion resistance, and clearance control. The "mating" of the alternating layers can increase the

resistance to dislocation for the entire composite structure, thereby decreasing the potential for coating failure. For example, when “plastic flow” in the relatively ductile, metallic layers is constrained by the more brittle ceramic layers, crack growth through the coating structure is also constrained. Since crack growth often signals the beginning of coating degradation, the “blunting” of these cracks can help to preserve coating integrity.

In brief, some of the preferred coating materials for the alternating structure are provided in claims 2 and 3, covering metals and ceramics, respectively. Preferred thicknesses for the individual and collective coatings are provided in claims 4-7, based in part on the balancing of properties, as noted above. Claim 12 is directed to a substrate (e.g., the turbine component of claim 20) on which the coating system is disposed. Claim 22 describes a method for making the nano-multilayered structure. Some of the preferred deposition systems, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), sputtering, and thermal spray techniques, are recited in claims 31-40. Claims 42-45 are directed to heat treatments which are sometimes undertaken after deposition of the various layers.

Fukui is directed to coating tools, in which multiple coating layers are applied over a base part. As described in paragraph 18 of the publication, one or more layers of a TiSi compound is applied over the base part, followed by the deposition of a film which includes a metal compound. The TiSi compound for the first layer(s) appears to be in the form of a nitride, carbide, carbonitride, oxynitride, or carboxynitride. The second film is a nitride, carbide, carbonitride, oxynitride, or carboxynitride of a metal selected from Ti, Cr, and TiCr.

Applicant submits that the pending claims are not anticipated by Fukui. The patent publication fails to describe a structure which includes alternating layers of a metallic alloy and a ceramic oxide. In fact, Fukui shows the deposition of ceramic materials over ceramic materials. Those skilled in the art would recognize that the cutting tools described in the publication require ceramic structures in order to perform the required machining and cutting functions.

Some of the Examiner's points in the Section 112 rejections appear to be somewhat relevant in this context as well, since they relate to the definitions of "metal", "metal alloy", and "ceramic". The undersigned appreciates some of the Examiner's questions in this regard, since it is true that in some instances, the boundary between ceramics and metals is not quite as clear as in other instances. However, it is well-established that ceramic compounds often include metals, yet they are clearly termed "ceramic". In fact, it would appear that, as a general rule, all ceramics contain either a metal, or a compound like silicon or carbon. (Again, the Hawley text mentioned above provides a variety of useful definitions for these terms). Many (though not all) of the ceramics fall into certain categories which support the classification, e.g., being in oxide form, and/or having very high refractory characteristics (often much higher than their metal "counterpart").

In the present case, the Examiner refers to the CrCNO layer of Fukui as the "ceramic layer". Applicant agrees that such a compound might be termed a ceramic material (even though it does contain a metal element as well). However, the Examiner then refers to the TiSiCNO layer as being the "metal alloy". While such a compound might be termed a "ceramic", it would not traditionally be called a "metallic alloy", in the way that claim 1 recites that term. (Nitrides and titanium nitrides – as materials of the prior art – were discussed at length in the specification. That discussion will be reviewed in a subsequent section of this Response). Applicant thus submits that claim 1 is not anticipated by Fukui. The claims dependent from claim 1 are also not anticipated by the reference. Moreover, the elements of independent claims 12 and 22 are also not disclosed by Fukui. Therefore, these claims, as well as the rejected claims dependent therefrom, are also patentable in view of Fukui.

Applicant also makes note of the status of Fukui as a reference. Fukui has a publication date of January 29, 2004, and a foreign application filing date of July 11, 2002. While the reference is clearly distinguishable from the pending claims in terms of subject matter, it also has an effective date which is after the date of invention for the present Application. If the need arises, Applicant would be prepared to remove the reference by an appropriate procedural mechanism.

Claims 1, 3-9; 12, 14-19; 22, 24-29; 31-32; 36-37; and 42-45 have been rejected under 35 U.S.C. 102(b). The reference applied here is U.S. Patent 6,333,099, issued to C. Strondl et al ("Strondl"). This patent also relates to cutting tools. The tool includes a substrate/"body", on which a laminar, multi-layer coating is deposited. It appears that layers of MLX/Al₂O₃ are alternated with separate layers of MLX and Al₂O₃ (alumina). The "MLX" name designates metal nitrides or metal carbides, where "M" and "L" individually designate metals such as Ti, Nb, Hf, V, Cr, W, etc. (See column 2, line 63 to column 3, line 16 of the patent).

Applicant emphatically submits that Strondl cannot be used for a rejection of claim 1, since the reference fails to contain the necessary elements of the claim. Strondl is clearly depositing ceramic layers over ceramic layers. As discussed before, materials like alumina (aluminum oxide) are clearly ceramic, regardless of whether they happened to contain a metal element. Moreover, the MLX materials (e.g., TiAlN) which the Examiner appears to designate as metal alloys are also more accurately designated as ceramics. Clearly, Strondl is describing ceramic composites – the standard for cutting tools. Applicant notes, for example, that the patent never refers to pure metal compositions or pure metal alloys, e.g., the materials exemplified in claim 2 of the present Application.

The argument set forth above is also relevant to rejected claims 12 and 22, which rely on the limitation of alternating metallic and ceramic layers. Moreover, the dependent claims set forth by the Examiner are also patentable, in view of the elements of claims 1, 12 and 22. As an example, claims which recite specific coating deposition techniques and specific layer thicknesses also rely on the presence of the multi-layer coating system, which provides the advantages described above.

Claims 1, 3, 4-12; 14-22; 24-32; 36-37; 41-42, and 45 have also been rejected under 35 U.S.C. 102(b), based on U.S. Patent 5,687,679, issued to Mullin et al ("Mullin"). The patent describes a "multiple nanolayer coating system". The

coating system is made of many thin layers of ceramic applied to a superalloy substrate (col. 2, lines 43-50).

Mullin certainly describes a coating system for turbine components. However, the reference is clearly missing elements which represent key features of the present invention. The coating system in the patent is ceramic-over-ceramic. Applicant respectfully, but strenuously, disagrees with the Examiner's characterization of a stabilized zirconia layer being equated to a "metal alloy layer" (see paragraph 13 of the Office Action, third sentence). Yttria-stabilized zirconia is well-known in the art as a ceramic layer, regardless of the presence of metal elements in the formula. This particular material is very popular in the industry as a ceramic overcoat for turbine components. A section of the patent (col. 4, lines 15-21) is instructive in this regard: "We have identified three ceramic materials which appear to be ideally suited...These are alumina, ...stabilized zirconia, ...and ceria...".

Claims 12 and 22 are also patentable over Mullin, for similar reasons. There are other distinctions in subject matter, between the reference and the claims of the present invention. In brief, however, the various dependent claims, which all rely indirectly on the specific multi-layer structure of the main embodiment, are clearly patentable over Mullin.

Rejections Under 35 U.S.C. 103

Claims 33-35 and 38-40 have been rejected as being unpatentable over the Mullin patent, referenced above, based on a theory of obviousness. Applicant has described various features of Mullin, and the Examiner also refers to specific portions of the reference in the Section 103 rejection. In general, there is no dispute as to the factual description set forth by the Examiner.

However, Applicant submits that the reference, as a whole, fails to describe or suggest the claimed invention. The claims at issue relate to the application of the multi-layer coating system by a thermal spray technique. However, a signal feature of those claims is the specific deposition of an

alternating collection of metal alloy and ceramic oxide layers, as recited in independent claim 22. Mullin has nothing to do with the deposition of such a coating structure. Instead, the reference appears to be concerned only with the deposition of a ceramic layer, i.e., the top layer of a turbine coating system. Regardless of whether that top layer in Mullin is formed from one or more sub-layers, the reference fails to suggest the present invention. Moreover, the suggestion that Mullin may somehow imply that other coating techniques could be used in no way supplies missing features present in the pending claims.

Claims 1, 3-9; 12, 14-19; 22, 24-29; 31-32, 35-37; 40, and 42-45 have been rejected as being unpatentable over Strondl (referenced previously). It is the Examiner's position that it would have been obvious to one of ordinary skill in the art to fabricate the articles of Strondl by chemical vapor deposition. (Page 8 of the Office Action). Applicant does not believe that the reference supports such a rejection.

Strondl has been described in some detail above. Again, the patent fails to suggest the key feature of the present invention, and is instead aimed at the deposition of ceramic layers over other ceramic layers. While the Examiner equates the TiAlN layer to Applicant's "metal alloy" layer, the technological state of the art would characterize such a layer as not being metallic in nature.

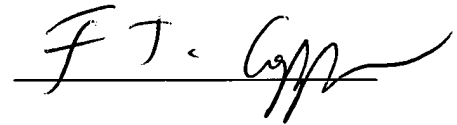
Moreover, Applicant specifically teaches against the use of that type of composition as the primary component for the present invention. As described in detail in paragraph 12 of the specification, cutting tool materials like Ti-TiN, TiN-TiAlN, TiN-NbN, and the like are used specifically as layer components in the cutting tool industry. However, such layers are often unsuitable for use at temperatures above about 600°C, because of their oxidation tendencies. Moreover, the use of those materials presents problems for various other substrates as well, as described in the last sentence in the paragraph. In contrast, Strondl not only fails to suggest the particular metal/ceramic oxide alternating structure of the present invention, but also fails to recognize the need for such a system in a high-temperature environment (e.g., hot gas paths for turbines) which presents a different set of requirements from those of the cutting tool industry.

The Examiner refers to various other features which are supposedly suggested by Strondl. However, Applicant maintains that similarities in features like deposition technique are of no particular importance when the reference fails to suggest the critical underlying features of the present invention. Certainly, decisions regarding coating equipment and layer thickness are dependent in part on layer composition and structure, yet Strondl clearly cannot provide such parameters, without any recognition of the coating structure in the first place.

Conclusion

Applicant believes the current claims are in condition for allowance, in view of this Response. However, the undersigned would be very willing to discuss any remaining matters with the Examiner, if such a discussion can remove any further issues regarding the allowance of this case. A telephone number has been provided below.

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Date: March 13, 2006

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